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14 (CHM-1) 106

2018

CHEMISTRY

Paper : CH 106

(Symmetry and Group Theory in Chemistry)

Full Marks : 40

Time : 2 hours

The figures in the margin indicate full marks for the questions.

1. Show that the four elements in $\{1, -1, i, -i\}$ constitute a mathematical group. 2
2. Answer **any two** of the following *three* questions : $2 \times 3 = 6$
 - (i) Define 'symmetry element'. What are the various symmetry elements that are present in the molecule CH_4 having a tetrahedral geometry ? $1 + 2 = 3$
 - (ii) Determine symmetry point groups for
 - (a) PF_5 in its two plausible geometries
 - (b) H_2 and H_2O_2
 - (c) The octahedron and the cube. $1 + 1 + 1 = 3$

Contd.

- (iii) What are classes of symmetry operations? Explain how classes correspond directly to the sets of equivalent operations. 3

3. Answer **any two** of the following **three** questions: 2×4=8

- (i) Define representation of a group. Derive the following relationship between any reducible representation of a group and the irreducible representations of that group. 1+3=4

$$a_i = \frac{1}{h} \sum_R \chi(R) \chi_i(R)$$

symbols carry their usual meaning.

- (ii) What are the *five* important rules about irreducible representations and their characters? Using these rule, determine the dimensions of the possible representations of the point group C_{2v} . 3+1=4

- (iii) Consider the following table and explain the four areas indicated by I, II, III and IV. 4

C_{2v}	E	$2C_2$	$2\sigma_v$		
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	-1	R_z	
E	2	-1	0	$(x, y)(R_x, R_y)$	$(x^2 - y^2, xy)(xz, yz)$
II	I	III	IV		

4. Determine the irreducible representations spanned by the genuine normal vibrations: for the *trans*- N_2F_2 molecule. Which of these vibration modes are Raman-active or IR active? Use the following character table, if necessary. 5

C_{2h}	E	C_2	σ_h	i	
A_g	1	1	1	1	R_z
B_g	1	-1	1	-1	R_x, R_y
A_u	1	1	-1	-1	z
B_u	1	-1	-1	1	x, y

or

Show that the stretching modes of vibration for the CO_3^{2-} anion reduce to $A_1' + E_1'$, whereas the in-plane modes of bending for the molecule contribute to E' only. Use the following character table, if necessary. 5

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_6$	$3\sigma_v$	
A_1'	1	1	1	1	1	1	$x^2 + y^2, z^2$
A_2'	1	1	-1	1	1	-1	R_z
E'	2	-1	0	2	-1	0	(x, y)
A_1''	1	1	1	-1	-1	-1	
A_2''	1	1	-1	-1	-1	1	z
E''	2	-1	0	-2	1	0	(R_x, R_y)

5. Give an overview of the various ways in which group theory finds application in quantum mechanics. 4

or

Using the following character table show that the direct product A_1EB_2 cannot be reduced in terms of the totally symmetric irreducible representation whereas the direct product E^2 can be reduced in terms of the totally symmetric representation.

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$		
A_1	1	1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	1	-1	-1	R_z	
B_1	1	-1	1	1	-1		$x^2 - y^2$
B_2	1	-1	1	-1	1	xy	
E	2	0	-2	0	0	$(x, y)(R_x, R_y)$	(xz, yz)

6. Show that the $\delta \rightarrow \delta^*$ transition in the $MO_2Cl_8^{4-}$ cation is electric-dipole allowed with z polarization and forbidden for radiation with electric vector in the xy plane. Use the following character table, if necessary.

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1	R_z	$x^2 + y^2, z^2$
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1		
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1		$x^2 - y^2$
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1	xy	
E_g	2	0	-2	0	0	2	0	-2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	z	
B_{1u}	1	-1	1	1	-1	-1	1	-1	1	-1		
B_{2u}	1	-1	1	-1	1	-1	1	-1	-1	1		
E_u	2	0	-2	0	0	-2	0	2	0	0	(x, y)	

or

Construct the symmetry adapted linear combinations (SALCs) of atomic orbitals for the SiF_4 molecule and show the possible bonding and antibonding combinations for the formation of the molecular orbitals (MOs). Use the following character table, if necessary.

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	linear functions, rotations	quadratic functions	cubic functions
A_1	+1	+1	+1	+1	+1	-	$x^2 + y^2 + z^2$	xyz
A_2	+1	+1	+1	-1	-1	-	-	-
E	+2	-1	+2	0	0	-	$(2x^2 - x^2 - y^2, x^2 - y^2)$	-
T_1	+3	0	-1	+1	-1	(R_x, R_y, R_z)	-	$[x(x^2 - y^2), y(x^2 - x^2), z(x^2 - y^2)]$
T_2	+3	0	-1	-1	+1	(x, y, z)	(xy, xz, yz)	$[x^3 - y^3, x^3 - y^3, y(x^2 - x^2), z(x^2 - y^2)]$

7. Answer **any two** of the following three questions : 2×4=8

- Discuss the similarities and differences of crystallographic symmetry with molecular or point symmetry. 4
- Define 'unit cell' in crystals and draw a generalized unit cell marking the cell parameters and faces in it. What are the minimum symmetry requirements for the unit cells of the seven crystal systems? 2+2=4

(iii) Draw an illustration for the glide operation in crystallographic symmetry. What are the various types of glide planes and their associated translational components ? $2+2=4$

(iv) Define space group and explain how the determination of space group is essential in crystal structure determination. State what are meant by P , 2_1 and c present in the space group symbol ' $P2_1/c$ '.

$$3+1=4$$